

**COMBINED RESULTS OF STUDIES ON
PRESERVATION TIME OF
ORGANOCHLOROPESTICIDES,
POLYCHLOROBIFENYLS AND
CHLOROBENZENES IN GROUND WATER,
WASTE WATER AND SURFACE WATER**

Versie 2

Fenelab
H. de Kok
September 2011

CONTENT

SUMMARY	3
1. INTRODUCTION.....	4
2. EXPERIMENTAL PROCEDURE	5
3. SAMPLE DESCRIPTION	7
4. DESCRIPTION OF METHODS.....	7
5. RESULTS.....	8
6. DISCUSSION	9
6.1. Ground water	9
6.2. Waste water	10
6.3. Surface water	12
7. CONCLUSIONS	13
8. LITERATURE	15

Attachement A

Attachement B

SUMMARY

In this report the results of studies on the preservation time of Organochloropesticides (OCPs), Polychlorobifenyls (PCBs) and Chlorobenzenes (CBs) in ground water, waste water and surface water are combined and evaluated.

Research was done by four environmental laboratories for preservation times of OCPs, PCBs and CBs in ground water and waste water. The results were widened with data of surface waters, which were obtained as part of the preparation of samples for interlaboratory collaborations.

The results discussed in this report indicate that, when samples are stored between 1-5 °C, the preservation time of ground water, waste water and surface water samples is at least 7 days for all OCPs, PCBs and CBs.

1. INTRODUCTION

Part of preservation times listed in environmental standards is not based on experimental data and/or research studies. In 2003 Fenelab members, under guidance of the SIKB, performed studies on the preservation time for a number of analysis/matrix combinations. The experimental set-up was laid out in the research program “Validatie van conserveringstermijnen van milieumonsters” (SIKB, april 2003)” [6]. The expectation that extended preservations times could be established, was confirmed for a number of analyt/matrix combinations.

Further studies on validation of preservation times were performed in 2008 to 2010. These studies [1], [2], [5], [7] were done by four laboratories on the basis of the protocol used in 2003 [6] and concerned Organochloropesticides (OCPs), Polychlorobifenyls (PCBs) and Chlorobenzenes (CBs) in ground water and waste water.

This report combines the outcome of the four studies mentioned above and also takes into account additional data on OCPs, PCBs and CBs in surface waters. The latter data were obtained in two studies as part of the preparation of samples for interlaboratory collaborations and are presented in this report or elsewhere [4].

In this report the experimental set-up, the samples used and the results are given for one of the studies on homogeneity and stability of samples for interlaboratory collaborations. The results of all of the studies are discussed and overall conclusions are drawn for the different compounds and water matrices described.

2. EXPERIMENTAL PROCEDURE

The experimental procedure used by the four laboratories for study on OCPs, PCBs and CBs in ground water and waste water is presented in the reports [1], [2], [5] and [7]. In these studies the experimental set-up was based on the research program "Validatie van conserveringstermijnen van milieumonsters" (SIKB, april 2003) [6]. Some adjustments of the original research program are described in the individual reports.

The experimental procedure used in successive years to study the homogeneity and stability of spiked surface waters, as part of the preparation of samples for interlaboratory collaborations (RWS Waterdienst studies, data presented here), was as follows.

- Each year 16 bottles were filled from one sample of surface water.
- All bottles were spiked with a solution of OCPs, PCBs and CBs (different levels in different years).
- 8 Samples were analysed after 0 days of storage.
- 8 Samples were analysed after 7 days of storage.

The experimental procedure used in one other study for establishing the homogeneity and stability of spiked surface water, as part of the preparation of samples for interlaboratory collaborations (KIWA, data presented in [4]), is described in detail in [3]. Ten bottles with the same spiked surface water were analysed after 0 days of storage and ten bottles were analysed after 8 days of storage.

The table below specifies the compounds measured in the different studies.

Compounds	Studies on preservation time	Study on stability of samples for interlaboratory collaborations	Study on stability of samples for interlaboratory collaborations
	References [1] [2] [5] [7]	This report	Reference [4]
Chlorobenzenes			
1,3,5-trichlorobenzene	X		
1,2,4-trichlorobenzene	X		
1,2,3-trichlorobenzene	X		
1,2,3,5+1,2,4,5-tetrachlorobenzene	X		
1,2,3,4-tetrachlorobenzene	X		
pentachlorobenzene	X	X	
hexachlorobenzene	X	X	X

Combined results of studies on preservation time of organochloropesticides, polychlorobiphenyls and chlorobenzenes
in ground water, waste water and surface water

Compounds	Studies on preservation time	Study on stability of samples for interlaboratory collaborations	Study on stability of samples for interlaboratory collaborations
Pesticides			
hexachlorobutadiene	X	X	
α-HCH	X	X	
β-HCH	X	X	
γ-HCH	X	X	X
δ-HCH	X	X	
heptachlor	X	X	X
aldrin	X	X	
telodrin	X	X	
isodrin	X	X	
cis-heptachlorepoxyde	X	X	
trans-heptachlorepoxyde	X	X	X
o,p'-DDE	X	X	
trans-chlordane	X		
cis-chlordane	X		
α-endosulfan	X	X	
p,p'-DDE	X	X	X
o,p'-DDD	X	X	
dieldrin	X	X	X
endrin	X	X	
p,p'-DDD	X	X	
β-endosulfan	X		
o,p'-DDT	X	X	
p,p'-DDT	X	X	X
endosulfansulphate	X		
PCBs			
PCB28	X	X	
PCB52	X	X	
PCB101	X	X	
PCB118	X	X	
PCB153	X	X	
PCB138	X	X	
PCB180	X	X	

3. SAMPLE DESCRIPTION

Samples used by the four laboratories for study on OCPs, PCBs and CBs in ground water and waste water are described in the reports [1], [2], [5] and [7].

Samples surface water used in successive years for preparation of samples for interlaboratory collaborations, were taken from the "Ketelmeer" lake or the "Flevoland Randmeer" lake (RWS Waterdienst studies, data presented here).

The sample surface water used in one other study for preparation of samples for interlaboratory collaborations was river water (KIWA, data presented in [4]).

4. DESCRIPTION OF METHODS

The analyses methods used in the different studies were accredited according to NEN-EN-ISO/IEC 17025 and consisted of extraction, clean-up and measurement by GC-ECD/ECD or GC-MS.

Details about the methods used by the four laboratories for study on OCPs, PCBs and CBs in ground water and waste water are presented in the reports [1], [2], [5] and [7].

5. RESULTS

The results obtained by the four laboratories in their studies on OCPs, PCBs and CBs in ground water and waste water are presented in the reports [1], [2], [5] and [7].

The results on surface waters used in successive years for preparation of samples for interlaboratory collaborations are presented in attachment A.

The results on surface water used in one other study for preparation of samples for interlaboratory collaborations are presented in [4].

6. DISCUSSION

Below the results are discussed per matrix.

6.1. Ground water

Both studies on ground water ([2] and [7]) show that for most compounds a preservation time of 14 days is adequate. With the exception of heptachlor, for which a preservation time of 10 days was found in both studies and with the exception of b-endosulfan for which a preservation time of 10 days was obtained in study [7].

The following criterion was used in the studies to evaluate the results:

- When two subsequent data points of the curve obtained, have a Z-value larger than -2 , the preservation time is exceeded.

Notes:

- Data points are expressed relative to day 0 (= 100%).
- $Z = ([\text{percentage of day } x \text{ relative to day } 0] - 100\%) / (\text{relative standard deviation})$
- The data point before the two with a Z-value larger than -2 , is the preservation time established.

The relative standard deviation to calculate the Z-value was based on method validation data or control chart data. For some compounds a relative standard deviation up to 25% was used ([2] and [7]). For these compounds the preservation time would only be shorter than the studied period of 14 days, in case concentrations dropped to less than 50% relative to day 0. For these cases the criterion, although statistically correct, was considered as large and leading to a possible overestimation of preservation times. Therefore in this report the data of both studies were also evaluated on the basis of the following criterion:

- When a data point of the curve obtained is less than 80%, the preservation time is exceeded.

Notes:

- Data points are expressed relative to day 0 (= 100%).
- Subsequent data points on the curve must also be less than 80%.

Based on this second criterion, the following conclusions are drawn:

- In both studies PCB118 and PCB153 have a preservation time of 10 days on the low addition level, 14 days on the high level.
- In study [2] b-endosulfan has a preservation time of 4 days and PCB138 of 10 days on the low addition level, 14 days for both on the high level. Hexachlorobenzene and o,p-DDT have a preservation time of 10 days on the high addition level, 14 days for both on the low level.

- In study [7] o,p-DDT, p,p-DDT and PCB180 have a preservation time of 10 days on the low addition level, 14 days on the high level.

Putting together the outcome of the evaluations on both the criteria, it can be seen that a preservation time of 10 days is adequate for all compounds in ground water and 14 days for the majority of the compounds. Only for b-endosulfan a preservation time of 4 days was obtained in one of the studies on one of the levels when applying the second criterion. Since this was not observed on all levels and studies and since the criterion was only slightly exceeded (96% on day 4, 79% on day 7 and 77% on day 10), it is not necessary to take this into account.

6.2. Waste water

Food industry

The studies on waste water from two food industries spiked at low level ([1] and [5]), done by two laboratories, show that for almost all compounds a preservation time of 10 or 14 days is adequate. With the exception of telodrin, for which a preservation time of 7 days was found in one study ([5]) and 4 days for p,p'-DDT in the other study ([1]). The evaluation was done based on the Z-value criterion (see 6.1). When the criterion of at least 80% relative to day 0 (see 6.1) is applied, for both studies exactly the same conclusions are drawn.

Municipal waste water treatment

The study on one sample of waste water from a municipal waste water treatment plant spiked at low and high level ([1]), done by one laboratory, shows that for most compounds a preservation time of 10 or 14 days is adequate. However for o,p-DDE, p,p'-DDE, o,p-DDT, p,p'-DDT, isodrin and aldrin a preservation time of 7 days is obtained, due to losses observed for the low level spike only. Evaluation of either the Z-value or 80% criterion, essentially leads to the same conclusions.

For PCBs, only spiked at low level, a decrease is observed after the first days of the experiment leading to levels below 80% at day 4 (PCB118, PCB138, PCB153, PCB180), day 7 (PCB101), day 10 (PCB52) and day 14 (PCB28). Thereafter concentrations stabilize around 80% (PCB28, PCB52), around 70% (PCB101) and around 60% (PCB138, PCB153, PCB180).

Other (industrial) waste water

The study on one sample of waste water from an industry spiked at low level ([5]), done by one laboratory, shows that for all compounds a preservation time of 14 days is adequate. The evaluation was done based on the Z-value criterion (see 6.1). When the criterion of at least 80% relative to day 0 (see 6.1) is applied, exactly the same conclusion is drawn.

The study on three samples of waste water from industries spiked at low level or high level ([1]), done by one laboratory, shows that for most compounds a preservation time of 10 or 14 days is adequate.

In the "first" waste water from industry, spiked at low level, hexachlorobutadiene decreased below 80% but recovered to more than 90% at 14 days. Aldrin decreases below 80% at day 7 and stabilizes at about 70%. β -Endosulfan decreases below 80% at day 2 and stabilizes at about 70%.

For PCBs no decrease in concentrations is observed.

In the "second" waste water from industry, spiked at high level, hexachlorobutadiene decreased below 80% but recovered to more than 90% at 14 days.

For PCBs concentrations drop below 80% at day 4 but stabilize around 80% thereafter.

In the "third" waste water from industry, spiked at low level, heptachlor decreases below 80% at day 2, concentrations stabilize from day 4 to 10 at about 60%. o,p'-DDT and p,p'-DDT decrease below 80% at day 4 and day 2 respectively, concentrations stabilize thereafter at about 50%. For aldrin, telodrin, isodrin, dieldrin and endrin concentrations decrease below 80% at day 4 and stabilize thereafter at about 70% for aldrin, telodrin and isodrin, about 80% for dieldrin and about 40% for endrin.

β -Endosulfan decrease below 80% at day 4 and stabilizes at about 70%.

For PCBs a decrease is observed after the first days of the experiment leading to levels below 80% at day 2 (PCB101, PCB118, PCB138, PCB153, PCB180) and day 4 (PCB28, PCB52). Thereafter concentrations stabilize around 70% (PCB28, PCB52, PCB101, PCB138), around 65% (PCB138, PCB153) and around 55% (PCB180).

Waste water – Overall observations

No relevant effects were observed for CBs in any of the waste water types and samples studied.

For OCPs most compounds are shown to be stable for at least 10 days. Heptachlor, aldrin, telodrin, isodrin, dieldrin, endrin, o,p'-DDE, p,p'-DDE, o,p'-DDT, p,p'-DDT and β -endosulfan, are shown to be stable for at least 7 days, although p,p'-DDT in one out of two samples of the food industry on low level spike and heptachlor, telodrin, isodrin, dieldrin, endrin, o,p'-DDE, p,p'-DDE, o,p'-DDT and p,p'-DDT in one out of three samples and aldrin and β -endosulfan in two out of three samples of waste water of industries showed losses before day 7. This however was not consistent over all samples and spike levels, therefore a preservation time of 7 days was considered adequate for these compounds.

For PCBs no relevant effects were observed for the samples of the food industry by both laboratories. In one waste water from industry the performing laboratory did not observe any effects. The other laboratory found a substantial decrease in concentrations for only the low level spikes of waste water of industries and only for one out of two samples. However, this was also seen for the sample of a municipal waste water treatment plant. The laboratory observed that relative large amounts of suspended matter were present in these samples. It is assumed that adsorption of spiked PCBs to the suspended matter caused the decrease in concentrations. This is supported also by the fact that losses are highest for the PCB with the highest number of chlorine atoms. Spiking creates of course an artificial sample, the observed effects in relation to preservation of samples, may well be relevant only for spiked samples. To further study the effect of adsorption of spiked compounds an additional experiment was performed which is described in attachment B. This experiment clearly shows that substantial levels of spiked PCBs (and some OCPs) which also increase in time, are found on

particles and the wall of the glass container and are not "available" any more by the standard extraction method. Thereby apparently giving a decrease in concentration in the sample, which in fact is not real.

Based on the discussion above and the results of the additional experiment, it was concluded that a preservation time of 7 days for PCBs in waste water can be applied.

6.3. Surface water

From the results on surface waters used in successive years for preparation of samples for interlaboratory collaborations (attachment A), it shows that the larger part of the percentages of day 7 relative to day 0 lie between -90% and +110%, a limited number lie between 80% and 90% or 110% and 120%. Three of the percentages of day 7 relative to day 0 lie between 70% and 80% (o,p-DDT, PCB138 and PCB153). Per compound there is no clear connection between the data of different years. It appears that increase or decrease in concentrations is somewhat random over the compounds and over the four years studied. It is known that the OCPs, PCBs and CBs analysis is sensitive for day to day effects, which can easily lead to differences in the order of 10%. Statistical evaluation with only two days to compare (no trend observation), is therefore considered not useful. Overall there is no clear indication that substantial losses occur in surface water for the compounds studied.

In the results on one surface water used in one other study for preparation of samples for interlaboratory collaborations [4], the percentages of day 8 relative to day 0 lie between 93% and 123%. There is no indication that substantial losses occur in the spiked surface water sample for the compounds studied.

7. CONCLUSIONS

The results of the studies combined in this report show that the preservation time of ground water, waste water and surface water samples is at least 7 days for all OCPs, PCBs and CBs, when water samples are stored between 1-5 °C before analysis.

Details for each compound are given in the table below.

Compound	Preservation time (days)		
	ground water	waste water	surface water
Chlorobenzenes			
1,3,5-trichlorobenzene	14	10	-
1,2,4-trichlorobenzene	14	10	-
1,2,3-trichlorobenzene	14	10	-
1,2,3,5+1,2,4,5-tetrachlorobenzene	14	10	-
1,2,3,4-tetrachlorobenzene	14	10	7
pentachlorobenzene	14	10	7
hexachlorobenzene	10	10	8
Pesticides			
hexachlorobutadiene	14	10	7
α-HCH	14	10	7
β-HCH	14	10	7
γ-HCH	14	10	8
δ-HCH	14	10	7
heptachlor	10	7	8
aldrin	14	7	7
telodrin	14	7	7
isodrin	14	7	7
cis-heptachlorepoxyde	14	10	7
trans-heptachlorepoxyde	14	10	8
o,p'-DDE	14	7	7
trans-chlordane	14	10	-
cis-chlordane	14	10	-
α-endosulfan	14	10	7
p,p'-DDE	14	7	8
o,p'-DDD	14	10	7
dieldrin	14	7	8

Combined results of studies on preservation time of organochloropesticides, polychlorobifenyls and chlorobenzenes
in ground water, waste water and surface water

endrin	14	7	7
p,p'-DDD	14	10	7
b-endosulfan	10	7	-
o,p'-DDT	10	7	7
p,p'-DDT	10	7	8
endosulfansulphate	14	10	-
PCBs			
PCB28	14	7	7
PCB52	14	7	7
PCB101	14	7	7
PCB118	10	7	7
PCB153	10	7	7
PCB138	10	7	7
PCB180	10	7	7

8. LITERATURE

- [1] van BAKERGEM, E, Validation of the preservation time of organochloro pesticides (OCP), polychloro bifenyls (PCB) and non-volatile chlorobenzenes (NCBZ) in waste waters, April 2011
- [2] BROER, W, VAL10236: Validation "Preservation time organochlorine pesticides, PCB and tri-, tetra-, penta- and hexachlorobenzene in groundwater", October 2008
- [3] KIWA Handboek RO hoofdstuk 6, Ringonderzoeken, Validatie van (nieuwe) parameters en/of matrices
- [4] KIWA, validatie t.b.v. ringonderzoeken, chloorpesticiden in water
- [5] LANDWEHR J, L, Validatie van conserveringstermijnen in Afvalwater. Houdbaarheid van OCB, PCB en CB (chloorbenzenen), February 2011
- [6] SIKB, Onderzoeksprogramma validatie van conserveringstermijnen van milieumonsters. SIKB project 55 Versie 10, April 2003
- [7] TUIN, G, Validation of the preservation time of organochloropesticides, polychlorobifenyls and chlorobenzenes in groundwater, August 2009

Note: all the documents above can be found at www.sikb.nl.

Combined results of studies on preservation time of organochloropesticides, polychlorobifenyls and chlorobenzenes
in ground water, waste water and surface water

ATTACHMENT A Results on surface waters used in successive years for preparation of samples for
interlaboratory collaborations

Compounds	2004											
	spike (RO 313) ug/l	serie 1 (day 0)					serie 2 (day 7)					day 7 rel. to day 0 (%)
		n	average ug/l	recovery %	Sw ug/l	VC (%) (%)	n	average ug/l	recovery %	Sw ug/l	VC (%) (%)	
2,4-DDD (o,p-DDD)	0.13	8	0.123	95	0.00745	6.1	8	0.112	86	0.01135	10.2	91
4,4-DDD (p,p-DDD)	0.13	8	0.121	93	0.00697	5.8	8	0.106	82	0.01586	14.9	88
2,4-DDE (o,p-DDE)	0.13	8	0.133	103	0.00735	5.5	8	0.126	97	0.00975	7.7	94
4,4-DDE (p,p-DDE)	0.13	8	0.113	87	0.00718	6.4	8	0.100	77	0.01193	11.9	89
2,4-DDT (o,p-DDT)	0.13	8	0.140	108	0.00991	7.1	8	0.100	77	0.00558	5.6	71
4,4-DDT (p,p-DDT)	0.13	8	0.139	107	0.00958	6.9	8	0.111	85	0.02491	22.4	80
aldrin	0.13	8	0.112	86	0.00529	4.7	8	0.108	83	0.00350	3.2	97
dieldrin	0.13	8	0.119	91	0.00707	6.0	8	0.112	86	0.00504	4.5	95
endrin	0.13	8	0.134	103	0.00841	6.3	8	0.136	105	0.00267	2.0	102
telodrin	0.13	8	0.122	94	0.00560	4.6	8	0.110	85	0.00385	3.5	90
isodrin	0.13	8	0.108	83	0.00565	5.2	8	0.106	81	0.00400	3.8	98
heptachloor	0.13	8	0.136	104	0.01306	9.6	8	0.116	89	0.01268	10.9	86
heptachloorepoxide (cis)	0.13	8	0.122	94	0.00643	5.3	8	0.119	92	0.00446	3.7	98
heptachloorepoxide (trans)	0.13	8	0.121	93	0.00665	5.5	8	0.118	90	0.00481	4.1	98
alfa-endosulfan	0.13	8	0.119	92	0.00639	5.4	8	0.104	80	0.00498	4.8	87
alfa - HCH	0.13	8	0.114	88	0.00601	5.3	8	0.117	90	0.00565	4.8	103
beta - HCH	0.13	8	0.123	95	0.00693	5.6	8	0.120	93	0.00673	5.6	98
gamma - HCH (lindane)	0.13	8	0.132	101	0.00712	5.4	8	0.128	99	0.00513	4.0	97
pentachloorbenzene	0.13	8	0.135	104	0.00785	5.8	8	0.120	93	0.00971	8.1	89
hexachloorbenzene	0.13	8	0.124	95	0.00712	5.7	8	0.124	96	0.00958	7.7	100
hexachloorethaan	0.13	8	0.101	77	0.00644	6.4	8	0.093	71	0.00652	7.0	92
hexachloorbutadiene	0.13	8	0.105	80	0.00661	6.3	8	0.104	80	0.00721	6.9	100
PCB - 28	0.13	8	0.123	95	0.00528	4.3	8	0.117	90	0.01267	10.9	95
PCB - 52	0.13	8	0.126	97	0.00612	4.9	8	0.126	97	0.00734	5.8	100
PCB - 101	0.13	8	0.122	94	0.00609	5.0	8	0.118	91	0.01087	9.2	96
PCB - 118	0.13	8	0.146	112	0.00896	6.2	8	0.130	100	0.01368	10.6	89
PCB - 138	0.13	8	0.132	102	0.00792	6.0	8	0.125	96	0.01879	15.0	95
PCB - 153	0.13	8	0.140	108	0.00836	6.0	8	0.133	103	0.01791	13.4	95
PCB - 180	0.13	8	0.132	101	0.00773	5.9	8	0.124	95	0.02187	17.7	94

Compounds	2005											
	spike (RO 344) ug/l	serie 1 (day 0)					serie 2 (day 7)					day 7 rel. to day 0 (%)
		n	average ug/l	recovery %	Sw ug/l	VC (%) (%)	n	average ug/l	recovery %	Sw ug/l	VC (%) (%)	
gamma - HCH (lindane)	0.31	8	0.319	103	0.00736	2.3	8	0.345	111	0.01299	3.8	108
pentachloorbenzene	0.31	8	0.366	118	0.00926	2.5	8	0.391	126	0.01497	3.8	107
PCB - 138	0.31	8	0.310	100	0.00645	2.1	8	0.307	99	0.02130	6.9	99
PCB - 153	0.31	8	0.309	100	0.00663	2.1	8	0.314	101	0.01938	6.2	101

Combined results of studies on preservation time of organochloropesticides, polychlorobifenyls and chlorobenzenes
in ground water, waste water and surface water

Compounds	2006											
	spike (RO 374) ug/l	n	serie 1 (day 0)				serie 2 (day 7)				day 7 rel. to day 0 (%)	
			average ug/l	recovery %	Sw ug/l	VC (%) (%)	n	average ug/l	recovery %	Sw ug/l		VC (%) (%)
2,4-DDD (o,p-DDD)	0.17	8	0.174	102	0.0089	5.1	8	0.184	108	0.0173	9.4	106
4,4-DDD (p,p-DDD)	0.17	8	0.177	104	0.0155	8.7	8	0.178	105	0.0220	12.3	100
2,4-DDE (o,p-DDE)	0.17	8	0.197	116	0.0085	4.3	8	0.194	114	0.0145	7.5	98
4,4-DDE (p,p-DDE)	0.17	8	0.170	100	0.0093	5.5	8	0.163	96	0.0156	9.6	96
2,4-DDT (o,p-DDT)	0.17	8	0.159	93	0.0088	5.5	8	0.181	106	0.0180	10.0	114
4,4-DDT (p,p-DDT)	0.17	8	0.167	98	0.0122	7.3	8	0.175	103	0.0195	11.1	105
aldrin	0.17	8	0.150	88	0.0042	2.8	8	0.150	88	0.0093	6.2	100
dieldrin	0.17	8	0.176	103	0.0054	3.1	8	0.185	109	0.0111	6.0	105
endrin	0.17	8	0.202	119	0.0119	5.9	8	0.206	121	0.0140	6.8	102
telodrin	0.17	8	0.166	97	0.0091	5.5	8	0.167	98	0.0109	6.5	101
isodrin	0.17	8	0.160	94	0.0044	2.7	8	0.152	90	0.0089	5.9	95
heptachloor	0.17	8	0.149	87	0.0107	7.2	8	0.144	84	0.0113	7.9	97
heptachloorepoxide (cis)	0.17	8	0.168	99	0.0046	2.7	8	0.174	102	0.0118	6.8	103
heptachloorepoxide (trans)	0.17	8	0.171	100	0.0060	3.5	8	0.174	102	0.0108	6.2	102
alfa-endosulfan	0.17	8	0.177	104	0.0068	3.9	8	0.164	97	0.0108	6.6	93
alfa - HCH	0.17	8	0.174	102	0.0088	5.0	8	0.155	91	0.0119	7.7	89
beta - HCH	0.17	8	0.175	103	0.0091	5.2	8	0.164	97	0.0135	8.2	94
gamma - HCH (lindane)	0.17	8	0.178	105	0.0085	4.8	8	0.159	93	0.0121	7.6	89
pentachloorbenzene	0.17	8	0.194	114	0.0080	4.1	8	0.200	118	0.0175	8.8	103
hexachloorbenzene	0.17	8	0.207	122	0.0109	5.3	8	0.206	121	0.0169	8.2	99
hexachloorethaan	0.17	8	0.132	78	0.0049	3.7	8	0.134	79	0.0111	8.3	102
hexachloorbutadiene	0.17	8	0.143	84	0.0041	2.9	8	0.146	86	0.0103	7.1	102
PCB - 28	0.17	8	0.190	112	0.0135	7.1	8	0.188	111	0.0174	9.3	99
PCB - 52	0.17	8	0.186	110	0.0186	10.0	8	0.210	123	0.0429	20.4	113
PCB - 101	0.17	8	0.179	105	0.0075	4.2	8	0.180	106	0.0154	8.6	100
PCB - 118	0.17	8	0.176	104	0.0111	6.3	8	0.200	118	0.0220	11.0	114
PCB - 138	0.17	8	0.179	105	0.0115	6.4	8	0.186	109	0.0197	10.6	104
PCB - 153	0.17	8	0.170	100	0.0090	5.3	8	0.186	110	0.0184	9.9	110
PCB - 180	0.17	8	0.162	96	0.0108	6.6	8	0.174	102	0.0198	11.4	107

Compounds	2007											
	spike (RO 407) ug/l	n	serie 1 (day 0)				serie 2 (day 7)				day 7 rel. to day 0 (%)	
			average ug/l	recovery %	Sw ug/l	VC (%) (%)	n	average ug/l	recovery %	Sw ug/l		VC (%) (%)
gamma - HCH (lindane)	0.38	8	2.450	645	0.1414	5.8	8	2.313	609	0.0641	2.8	94
hexachloorbenzene	0.38	8	0.410	108	0.0424	10.3	8	0.345	91	0.0316	9.2	84
PCB - 138	0.38	8	0.479	126	0.0380	7.9	8	0.348	91	0.0423	12.2	73
PCB - 153	0.38	8	0.493	130	0.0345	7.0	8	0.375	99	0.0431	11.5	76

ATTACHMENT B Results of an additional experiment on an effluent sample of a municipal waste water treatment plant

Introduction

The experiment was performed by the laboratory of Waterboard Groot Salland. The sample used was of the same municipal waste water treatment plant (Zwolle) as also used in study [1].

The experiment described below was set up after some exploratory tests, which showed that spiked PCBs and OCPs adsorb to sample particles and to sample containers and are not fully recovered by the standard extraction procedure. The experiment was designed to differentiate between PCBs and OCPs extracted from the original spiked sample on one hand and on the other hand PCBs and OCPs which remain after standard extraction on the particles and glass sample bottle.

Experimental

Nine 1 liter green glass bottles filled with 900 ml of sample were spiked at day 0 at a concentration of 0.18 µg/l. The sample contained suspended particles at a level common to this type of sample. The spike solution contained PCBs, OCPs and CBs.

Three spiked sample bottles were analyzed directly, three after 2 days and three after 7 days.

The first part of the sample pretreatment consisted of the following steps according to the standard procedure of the laboratory:

- transfer the sample to a 1000 ml separation funnel and add internal standard solution
- wash the empty sample bottle with 100 ml petroleum ether and add the petroleum ether to the sample in the separation funnel
- extract the sample two times with 100 ml of petroleum ether each time, by mechanical shaking for 5 minutes.

Additionally the following was done:

- the 200 ml petroleum ether extract plus any emulsion was collected in a centrifuge bottle
- the separation funnel was rinsed with water which was also collected in the centrifuge bottle (to include particles adhered to the wall of the separation funnel)
- the total liquid was centrifuged and next transferred to a 250 ml separation funnel
- with the separated petroleum ether phase the analysis was carried on according to the standard procedure of the laboratory.

- The separated water phase with particles was added to the extracted water sample (which also contained part of the particles)
- the combined water phase was filtered by use of a flow-through centrifuge equipped with a 1 µm glass fiber filter, particles were collected on the filter

- The empty original sample bottle was extracted by shaking for 10 minutes with 100 ml acetone and next 100 ml of petroleum ether
- both the acetone and the petroleum ether were used for extraction of the filter with particles (described above), according to the standard procedure of the laboratory for analysis of suspended material collected on a glass fiber filter.

The above sample pretreatment resulted in two extracts:

1. compounds extracted from the original spiked sample
2. compounds extracted from the suspended material plus compounds extracted from the glass sample bottle wall.

Both extracts were separately cleaned by aluminum oxide, concentrated and analyzed by GC-ECD/ECD procedures.

Results

For each day (0, 2 and 7) the average of three samples was calculated as recovery of the amount spiked of every compound in the original spiked sample and in the combined particle / glass wall extract.

The results are given in the table below.

Compounds	recovery original spiked sample			recovery extracted particles and glass wall		
	(%)			(%)		
	day 0	day 2	day 7	day 0	day 2	day 7
Chlorobenzenes						
1,3,5-trichlorobenzene						
1,2,4-trichlorobenzene						
1,2,3-trichlorobenzene						
1,2,3,5+1,2,4,5-tetrachlorobenzene	54.1	56.3	55.3	0.6	0.3	0.4
1,2,3,4-tetrachlorobenzene	60.1	60.8	60.9	0.5	0.5	0.4
pentachlorobenzene	62.7	62.7	63.8	0.5	0.5	0.6
hexachlorobenzene	65.8	66.4	65.7	0.6	1.1	1.1
Pesticides						
hexachlorobutadiene	44.2	56.5	57.6	0.3	0.3	0.3
a-HCH	76.5	79.1	76.3	0.9	0.5	0.6
b-HCH	80.8	85.4	82.8	0.9	0.7	0.9
γ-HCH	83.0	87.1	85.3	0.9	0.5	0.8

Combined results of studies on preservation time of organochloropesticides, polychlorobiphenyls and chlorobenzenes in ground water, waste water and surface water

Compounds	recovery original spiked sample			recovery extracted particles and glass wall		
	(%)			(%)		
	day 0	day 2	day 7	day 0	day 2	day 7
d-HCH						
heptachlor	72.2	74.1	66.4	0.9	3.1	3.9
aldrin	74.9	74.5	68.2	0.9	4.9	5.4
telodrin	81.3	79.7	73.4	1.1	3.0	3.8
isodrin	89.7	88.5	81.7	1.2	5.0	5.9
cis-heptachlorepoxyde	87.5	89.1	87.4	1.2	1.5	1.7
trans-heptachlorepoxyde	85.1	85.4	83.4	1.0	1.8	2.4
o,p'-DDE	85.8	78.4	72.7	1.3	7.0	9.2
trans-chlordane	86.3	82.4	76.9	1.1	5.1	6.5
cis-chlordane	84.7	82.3	76.9	1.0	4.4	6.0
a-endosulfan	87.8	88.1	86.0	1.1	1.3	1.5
p,p'-DDE	87.8	78.3	72.8	1.3	8.1	10.9
o,p'-DDD	89.2	81.3	75.3	1.3	6.4	8.7
dieldrin	85.9	86.2	83.1	1.1	1.7	2.5
endrin	86.8	86.7	84.8	1.1	1.3	1.7
p,p'-DDD	87.9	77.1	70.4	1.3	8.9	11.6
b-endosulfan						
o,p'-DDT	89.0	82.2	78.6	1.3	7.7	11.2
p,p'-DDT	99.3	91.4	88.9	1.4	10.1	14.8
endosulfansulphate						
PCBs						
PCB28	75.7	77.5	72.3	1.1	2.7	2.9
PCB52	79.8	76.4	70.5	1.0	5.8	6.8
PCB101	86.9	78.9	73.4	1.3	7.8	9.8
PCB118	90.3	79.8	75.2	1.4	7.6	9.8
PCB153	91.1	81.1	74.8	1.5	7.8	12.1
PCB138	89.6	78.8	74.6	1.4	8.2	12.5
PCB180	95.5	86.6	80.7	1.4	6.8	12.8

Conclusions

The results show that a considerable amount of the spike is adsorbed to the particles and glass sample bottle and is not extracted in the standard analysis. This is particularly the case for the PCBs, but also for some of the OCPs. The amount adsorbed increases in time, but is already substantial within two days.

In other experiments, not described here, it was observed that the larger part of the amount adsorbed is found on the particles and a smaller amount on the glass sample bottle.

It is likely that the nature and the amount of particles effects the amount adsorbed. The larger the amount of particles, the larger the apparent loss of PCBs and OCPs would be.